Origins of selectivity for the [2+2] cycloaddition of α,β-unsaturated ketones within a porous self-assembled organic framework.

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X-Ray Structure Determination, $C_{12}H_{16}O_2$

X-ray diffraction intensity data from a colorless prism crystal were measured at 150(1) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] Several crystals were surveyed, all of which were found to be twinned. The crystal selected for data collection was composed of two domains. Identification of the twinning and derivation of the twin law which transforms the indices of one domain into those of the other was performed with the Bruker program Cell_Now.[1] The twin law is

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.476 & -0.827 & 1 \end{pmatrix}$$

which corresponds to a 180° rotation about the reciprocal [001] axis. Integration of the twinned raw data frames was performed with SAINT+.[1] Reflection files for structure solution (SHELX HKLF 4 format) and twin refinement (SHELX HKLF 5 format) were created with TWINABS.[1] Final unit cell parameters were determined by least-squares refinement of 2043 strong reflections

from the major domain. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[2] The major twin fraction refined to 0.730(1).

The compound crystallizes in the triclinic system. The space group $P\bar{1}$ was confirmed by the successful solution and refinement of the data. The asymmetric unit consists of one complete molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference maps before being placed in geometrically idealized positions and included as riding atoms with refined isotropic displacement parameters.

(1) SMART Version 5.630, Cell_Now, SAINT+ Version 6.45 and TWINABS Version 1.05. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.

(2) Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

Table 1. Crystal data and structure refinement for mecpd.

Identification code	mecpd	
Empirical formula	C12 H16 O2	
Formula weight	192.25	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 6.4403(12) Å	α= 74.611(3)°.
	b = 6.8554(12) Å	β= 78.455(3)°.
	c = 12.826(2) Å	γ = 67.987(3)°.
Volume	502.97(16) Å^3	
Z	2	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	208	
Crystal size	0.32 x 0.14 x 0.10 mm^3	
Theta range for data collection	1.66 to 24.15°.	
Index ranges	-7<=h<=7, -7<=k<=7, 0<=l<=14	
Reflections collected	1899	
Independent reflections	1899 [R(int) = 0.0000]	
Completeness to theta = 24.15°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1899 / 0 / 146	
Goodness-of-fit on F^2	1.151	
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1183	
R indices (all data)	R1 = 0.0502, wR2 = 0.1213	
Largest diff. peak and hole	0.313 and -0.181 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mecpd. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2976(3)	6614(3)	2415(2)	21(1)
C(2)	4525(3)	4419(3)	2220(2)	19(1)
C(3)	3553(3)	3062(3)	1755(2)	20(1)
C(4)	5086(4)	2046(3)	821(2)	25(1)
C(5)	7071(4)	198(3)	1327(2)	28(1)
C(6)	6128(3)	-527(3)	2479(2)	22(1)
C(7)	4079(3)	1275(3)	2809(2)	21(1)
C(8)	4635(3)	2821(3)	3331(2)	21(1)
C(9)	2583(4)	4008(3)	4060(2)	25(1)
C(10)	2227(4)	6398(3)	3623(2)	26(1)
C(11)	1116(3)	4124(3)	1517(2)	27(1)
C(12)	6819(4)	1986(3)	3850(2)	28(1)
O(1)	2458(2)	8262(2)	1734(1)	28(1)
O(2)	6892(2)	-2289(2)	3064(1)	30(1)

Table 3. Bond lengths [Å] and angles [°] for mecpd.

C(1)-O(1)	1.209(2)
C(1)-C(10)	1.512(3)
C(1)-C(2)	1.516(3)
C(2)-C(8)	1.546(3)
C(2)-C(3)	1.580(3)
C(2)-H(2)	1.0000
C(3)-C(11)	1.518(3)
C(3)-C(4)	1.533(3)
C(3)-C(7)	1.561(3)
C(4)-C(5)	1.531(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.509(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-O(2)	1.219(2)
C(6)-C(7)	1.509(3)
C(7)-C(8)	1.568(3)
C(7)-H(7)	1.0000
C(8)-C(12)	1.522(3)
C(8)-C(9)	1.545(3)
C(9)-C(10)	1.528(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
O(1)-C(1)-C(10)	125.69(18)

O(1)-C(1)-C(2)	126.38(19)
C(10)-C(1)-C(2)	107.91(17)
C(1)-C(2)-C(8)	107.31(16)
C(1)-C(2)-C(3)	118.49(16)
C(8)-C(2)-C(3)	90.20(14)
C(1)-C(2)-H(2)	112.9
C(8)-C(2)-H(2)	112.9
C(3)-C(2)-H(2)	112.9
C(11)-C(3)-C(4)	111.98(16)
C(11)-C(3)-C(7)	117.91(17)
C(4)-C(3)-C(7)	105.71(15)
C(11)-C(3)-C(2)	115.96(16)
C(4)-C(3)-C(2)	114.45(16)
C(7)-C(3)-C(2)	88.62(14)
C(5)-C(4)-C(3)	106.57(16)
C(5)-C(4)-H(4A)	110.4
C(3)-C(4)-H(4A)	110.4
C(5)-C(4)-H(4B)	110.4
C(3)-C(4)-H(4B)	110.4
H(4A)-C(4)-H(4B)	108.6
C(6)-C(5)-C(4)	104.52(17)
C(6)-C(5)-H(5A)	110.8
C(4)-C(5)-H(5A)	110.8
C(6)-C(5)-H(5B)	110.8
C(4)-C(5)-H(5B)	110.8
H(5A)-C(5)-H(5B)	108.9
O(2)-C(6)-C(5)	125.78(19)
O(2)-C(6)-C(7)	124.60(19)
C(5)-C(6)-C(7)	109.62(17)
C(6)-C(7)-C(3)	105.97(16)
C(6)-C(7)-C(8)	113.78(17)
C(3)-C(7)-C(8)	90.10(14)
C(6)-C(7)-H(7)	114.7
C(3)-C(7)-H(7)	114.7
C(8)-C(7)-H(7)	114.7
C(12)-C(8)-C(9)	112.55(16)

C(12)-C(8)-C(2)	117.41(17)
C(9)-C(8)-C(2)	104.15(15)
C(12)-C(8)-C(7)	118.70(16)
C(9)-C(8)-C(7)	111.73(16)
C(2)-C(8)-C(7)	89.56(14)
C(10)-C(9)-C(8)	105.25(15)
C(10)-C(9)-H(9A)	110.7
C(8)-C(9)-H(9A)	110.7
C(10)-C(9)-H(9B)	110.7
C(8)-C(9)-H(9B)	110.7
H(9A)-C(9)-H(9B)	108.8
C(1)-C(10)-C(9)	105.19(16)
C(1)-C(10)-H(10A)	110.7
C(9)-C(10)-H(10A)	110.7
C(1)-C(10)-H(10B)	110.7
C(9)-C(10)-H(10B)	110.7
H(10A)-C(10)-H(10B)	108.8
C(3)-C(11)-H(11A)	109.5
C(3)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mecpd. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	20(1)	20(1)	27(1)	-5(1)	-5(1)	-10(1)
C(2)	17(1)	20(1)	19(1)	-5(1)	0(1)	-8(1)
C(3)	23(1)	18(1)	21(1)	-5(1)	-4(1)	-6(1)
C(4)	30(1)	21(1)	23(1)	-7(1)	-4(1)	-7(1)
C(5)	28(1)	24(1)	30(1)	-10(1)	-2(1)	-5(1)
C(6)	24(1)	18(1)	29(1)	-6(1)	-7(1)	-9(1)
C(7)	21(1)	20(1)	23(1)	-4(1)	-1(1)	-9(1)
C(8)	23(1)	19(1)	21(1)	-3(1)	-4(1)	-7(1)
C(9)	32(1)	25(1)	20(1)	-6(1)	1(1)	-12(1)
C(10)	28(1)	23(1)	26(1)	-9(1)	0(1)	-7(1)
C(11)	27(1)	24(1)	33(1)	-8(1)	-9(1)	-7(1)
C(12)	32(1)	25(1)	28(1)	-5(1)	-10(1)	-9(1)
O(1)	35(1)	19(1)	29(1)	-3(1)	-7(1)	-8(1)
O(2)	33(1)	20(1)	36(1)	-3(1)	-10(1)	-7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mecpd.

	x	y	z	U(eq)
H(2)	6046	4421	1849	21(5)
H(4A)	4257	1496	462	19(5)
H(4B)	5627	3121	272	18(5)
H(5A)	7619	-988	928	34(6)
H(5B)	8330	700	1318	50(8)
H(7)	2773	825	3202	27(6)
H(9A)	1233	3688	4010	36(6)
H(9B)	2891	3572	4830	23(5)
H(10A)	621	7279	3758	42(7)
H(10B)	3144	6867	3974	42(7)
H(11A)	1012	5263	859	38(6)
H(11B)	193	4747	2133	28(6)
H(11C)	569	3047	1406	30(6)
H(12A)	8086	1365	3333	23(5)
H(12B)	6734	879	4506	32(6)
H(12C)	7043	3176	4046	46(7)

Table 6. Torsion angles [°] for mecpd.

O(1)-C(1)-C(2)-C(8)	-179.04(19)
C(10)-C(1)-C(2)-C(8)	2.4(2)
O(1)-C(1)-C(2)-C(3)	-79.1(3)
C(10)-C(1)-C(2)-C(3)	102.3(2)
C(1)-C(2)-C(3)-C(11)	1.4(3)
C(8)-C(2)-C(3)-C(11)	111.25(18)
C(1)-C(2)-C(3)-C(4)	134.09(18)
C(8)-C(2)-C(3)-C(4)	-116.01(17)
C(1)-C(2)-C(3)-C(7)	-119.25(18)
C(8)-C(2)-C(3)-C(7)	-9.35(14)
C(11)-C(3)-C(4)-C(5)	-152.97(18)
C(7)-C(3)-C(4)-C(5)	-23.3(2)
C(2)-C(3)-C(4)-C(5)	72.4(2)
C(3)-C(4)-C(5)-C(6)	28.1(2)
C(4)-C(5)-C(6)-O(2)	157.7(2)
C(4)-C(5)-C(6)-C(7)	-22.5(2)
O(2)-C(6)-C(7)-C(3)	-172.06(18)
C(5)-C(6)-C(7)-C(3)	8.2(2)
O(2)-C(6)-C(7)-C(8)	90.6(2)
C(5)-C(6)-C(7)-C(8)	-89.2(2)
C(11)-C(3)-C(7)-C(6)	135.52(18)
C(4)-C(3)-C(7)-C(6)	9.4(2)
C(2)-C(3)-C(7)-C(6)	-105.61(16)
C(11)-C(3)-C(7)-C(8)	-109.65(18)
C(4)-C(3)-C(7)-C(8)	124.26(16)
C(2)-C(3)-C(7)-C(8)	9.22(14)
C(1)-C(2)-C(8)-C(12)	-108.17(19)
C(3)-C(2)-C(8)-C(12)	131.78(18)
C(1)-C(2)-C(8)-C(9)	17.0(2)
C(3)-C(2)-C(8)-C(9)	-103.03(16)
C(1)-C(2)-C(8)-C(7)	129.35(16)
C(3)-C(2)-C(8)-C(7)	9.30(14)
C(6)-C(7)-C(8)-C(12)	-23.2(2)
C(3)-C(7)-C(8)-C(12)	-130.79(18)

C(6)-C(7)-C(8)-C(9)	-156.79(17)
C(3)-C(7)-C(8)-C(9)	95.66(16)
C(6)-C(7)-C(8)-C(2)	98.13(18)
C(3)-C(7)-C(8)-C(2)	-9.42(14)
C(12)-C(8)-C(9)-C(10)	98.31(19)
C(2)-C(8)-C(9)-C(10)	-29.9(2)
C(7)-C(8)-C(9)-C(10)	-125.20(18)
O(1)-C(1)-C(10)-C(9)	160.3(2)
C(2)-C(1)-C(10)-C(9)	-21.1(2)
C(8)-C(9)-C(10)-C(1)	31.7(2)

Symmetry transformations used to generate equivalent atoms: